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THIRD QUARTERLY REPORT

by

R. PAPE

L. REED

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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THIRD QUARTERLY REPORT

(January - March 1966)

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AN INVESTIGATION OF SOLUBILITY AND DIFFUSION
OF OXYGEN IN REFRACTORY METALS

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ABSTRACT

Electrical resistivity measurements are being used to determine the solubility limits and diffusion constants of oxygen in tantalum, Ta-10W, alloy T222, columbium, Cb-1% Zr, and alloy FS-85.

Tentative solubility limits have been established for tantalum in the range 600 to 920°C. The limits of solubility range from 770 ppm at 598°C to 2265 ppm at 918°C.

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I. INTRODUCTION

This investigation concerns oxygen diffusion and solubility in commercially pure refractory metals and in advanced alloys for space power system components. Oxygen contamination of refractory metals reduces their resistance to alkali metal corrosion. Accurate knowledge of oxygen diffusion constants and solubility limits are required in order to establish realistic engineering and environmental specifications.

This investigation is divided into two phases:

Phase I. A determination of the limits of oxygen solubility in commercially pure tantalum and columbium and in the alloys Cb-1Zr, Ta-10W, FS-85 (Cb-28Ta-10.5W-0.9Zr) and T222 (Ta-9.8W-2.4Hf-0.01C), at five temperatures in the temperature range of 1000°F to 2400°F.

Phase II. Average diffusion constants will be determined from electrical resistivity data using commercially obtainable wires for specimen samples. Absolute oxygen contents shall be determined by neutron activation analysis. Other methods of analysis such as electron microprobe analysis, X-ray diffraction analysis, microhardness and conventional chemical analysis will be employed for obtaining corroborating data.

It is expected that the data obtained on the pure metals will confirm the previously reported data in the'

literature and provide the required confidence level to pursue alloy solubility data.

II. SUMMARY

A series of five oxygen calibration runs was completed and specimens were then submitted for neutron activation analysis. The results were used to construct an oxygen calibration curve to relate the change in resistance at constant temperature to the additive oxygen content in ppm.

A series of six iso-thermal solubility runs was completed. The data from these runs was used in conjunction with the oxygen calibration curve to yield the (tentative) solubility limits for oxygen in tantalum in the range 600°C to 920°C.

Two of the iso-thermal runs together with an iso-concentration run were conducted at extended time schedules to explore the time dependence of the data obtained from the two techniques.

III. APPARATUS

The apparatus employed in the solubility determination phase of this program is described in the 1st and 2nd quarterly reports.

A. Double Vacuum Furnace

A double wall vacuum furnace was built during the last quarterly period to supplement the air furnace used for the lower temperature range solubility runs. Early in this quarter the furnace proper (independent from the solubility determination apparatus) was pumped down and the heating elements powered.

Under power the tungsten heaters (0.050 diameter hair-pin filaments) twisted and were in jeopardy of shorting out through the weights hung from the filament loops. A ceramic guard ring was installed to correct this tendency.

B. Dense Alumina Reaction Tubes

Four dense alumina tubes were purchased to supplement the quartz reaction tubes, in use with the lower-temperature range air furnace. Of these, one was porous at the closed end, two were cracked during cutting operations and a fourth was metallized and brazed into a flange but developed a leak across the metallized area. The porous tube was returned to the vendor; the two tubes with cracks on the open end have been re-cut below cracks and will be metallized* with a metallizing paint which will be specifically

*Morganite ARR Alumina has not previously been metallized by us.

developed for this low silica ceramic body.

The ceramic tube in the flange has only a low order leak so it can be used in the double vacuum oven as there is sufficient pumping speed in the guard vacuum to protect the heater filaments.

IV. EXPERIMENTAL PROCEDURES

A. General

The experimental procedures employed in the work during this quarter were discussed in detail in the 2nd Quarterly Report.

The chemical cleaning procedure used on tantalum specimens is described in Table I.

Special procedures specific to individual runs or run categories are discussed more appropriately in the results section.

B. Vacuum Bake-out of Solubility Apparatus

The entire vacuum system of the oxygen solubility determination apparatus can be baked out and a base pressure of 1×10^{-9} achieved before starting each experimental run. This practice is not required, however, since the first charge will be adsorbed on the walls, sample holder, etc. and will make it impossible to regain a high vacuum without a long vacuum bake-out. Further, the oxygen adsorbed by the clean walls, etc. is diverted from the specimen so that the amount of oxygen accepted by the specimen varies

TABLE I

| CLEANING PROCEDURE FOR Ta SPECIMENS | |
|-------------------------------------|---|
| 1. | Vapor degrease (Trichlorethylene) |
| 2. | Rinse, de-ionized water |
| 3. | Immerse in acid mixture for 5 seconds (10% HF, 90% HNO ₃ by volume) |
| 4. | Rinse, de-ionized water |
| 5. | Rinse, C.P. ethanol |
| 6. | Static air dry |

over the first few charges even though the charges admitted may be identical and the sorption capacity constant. It was therefore deemed the preferable procedure to allow the walls, etc. of the apparatus to become and remain saturated with oxygen.

C. Time Correlation During Experimental Runs

A Moseley 680 "Autograph" recorder has been connected to the output of the "Millitorr" ionization gage (1 to 1×10^{-6} torr). The pressure-time profile provides a means of monitoring the engassing charge cycle; an event marker pen provides temporal correlation between the engassing cycle and the resistance-measurements taken on the Kelvin bridge.

V. EXPERIMENTAL RESULTS

A. General

A total of 13 experimental runs were conducted in this quarter. Five runs comprised an "oxygen calibration" series; six were oxygen solubility runs employing the iso-thermal technique; one run employed the iso-concentration technique; one iso-thermal run was completed with a Ta-10W specimen.

The iso-thermal and iso-concentration techniques have been discussed previously in the first and second quarterly reports.

B. Iso-Thermal Solubility Runs

A series of 5 iso-thermal runs were conducted to

determine the solubility limit of oxygen in Ta over the range 600°C to 950°C. The sample arrangement is as depicted in Figure 1. A photograph of an actual specimen is shown in Figure 4 of the Second Quarterly Report together with details of sample preparation. The isothermal technique requires that the solubility limit be indicated by a break in the resistance vs oxygen charge curve.

Experimental runs TA 05 through TA 09 employed the iso-thermal technique. The pre-treatment of the sample consisted of chemically cleaning the recrystallized wire as outlined in Table I and a vacuum bake-out at 900°C for a minimum of 12 hours unless noted otherwise in the text. Engassing was accomplished by trapping an oxygen charge in a 300cc volume at reduced pressure, pumping out the balance of the oxygen feed system and then admitting the charge to the reaction tube of the furnace through valve V⁵ (See Figure 2). Each charge cycle consisted of a 3 - 3/4 minute period during which the oxygen charge was admitted to the specimen and a second 3 - 3/4 minute period during which the reaction tube was pumped out and the specimen was allowed to homogenize. Resistance measurements were made during this second half of the 7 - 1/2 minute cycle.

The specimen weights, constant engassing temperatures and size of oxygen charge was varied from run to run as noted.

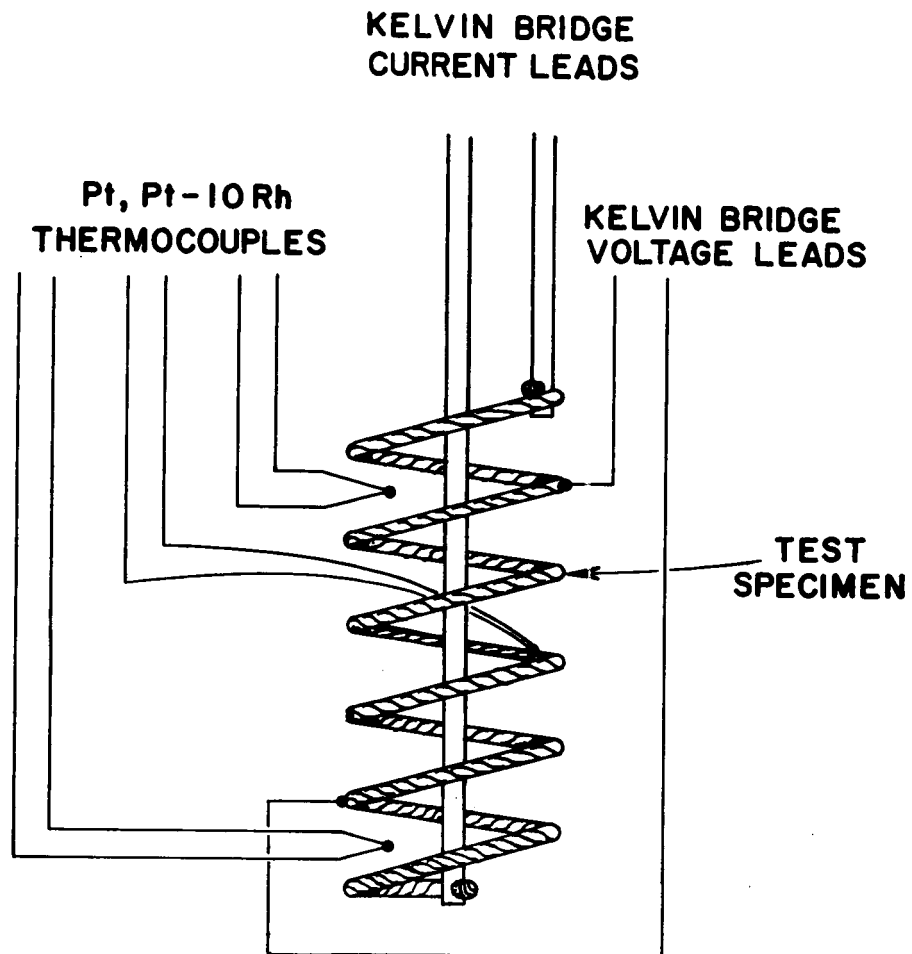
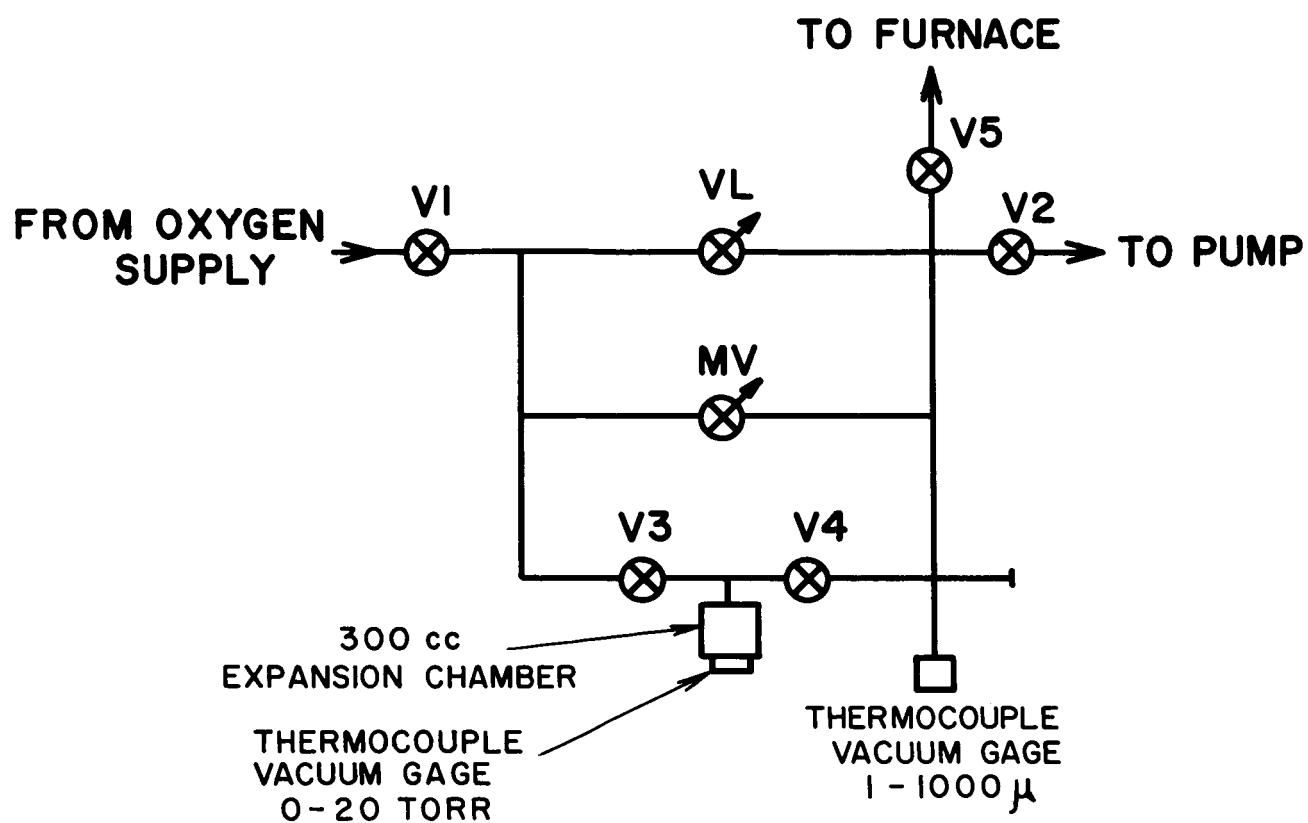


FIGURE 1. Schematic of Test Specimen showing placement of current and voltage leads and thermocouples.



MV : Micrometer metering valve
 VL : Granville - Phillips variable leak
 V : High vacuum bakable valves

FIGURE 2. Schematic of Oxygen Feed System.

Experimental Run TA 05

TA 05 was conducted at a constant temperature of 780°C. A total of 44 oxygen charges (300 cc at 1000 μ per charge) were admitted to the reaction tube. There were two procedural errors, occurring in the 2nd and 3rd cycle which were easily corrected during reduction of the data. The data are reported in Table II and the resistance vs oxygen charges admitted is plotted in Figure 3. Intersection of the initial and final linear portions of the curve occurs at approximately $R/R_0 = 1.205$ when correction is made for procedural errors. (The procedural errors such as to cause a deprivation of oxygen can be adjusted for by shifting the curve to the left by an appropriate amount. This correction does not effect R_s/R_0 , however.)

Experimental Run TA 06

TA 06 was conducted at a constant temperature of 881°C. A total of 33 oxygen charges were admitted to the reaction tube. The charge size was 300 cc at 2000 μ . This is double the charge size employed in the preliminary Run TA 05 and has been adopted as a "unit charge" hereafter. The solubility limit is indicated at $R/R_0 = 1.249$. (See Table III)

Experimental Run TA 07

TA 07 was conducted at a constant temperature of 598°C. A total of twenty-five 1000 μ charges was admitted to

TABLE NO. II

| Resistance Data From Run TA 05 | | | | | |
|---|----------|-------------------|--|----------|-------------------|
| Oxygen Charge No. | R (Ohms) | Normalized R R/Ro | Oxygen Charge No. | R (Ohms) | Normalized R R/Ro |
| 0 | .1912 | 1.000 | 23 | .2237 | 1.170 |
| 1 | .1919 | 1.037 | 24 | .2249 | 1.176 |
| 2 | .1920 | 1.004 | 25 | .2259 | 1.181 |
| 3 | .1932 | 1.011 | 26 | .2269 | 1.187 |
| 4 | .1947 | 1.018 | 27 | .2280 | 1.192 |
| 5 | .1962 | 1.026 | 28 | .2290 | 1.198 |
| 6 | .1978 | 1.035 | 29 | .2299 | 1.202 |
| 7* | .1982 | 1.037 | 30 | .2308 | 1.207 |
| 8 | .2000 | 1.046 | 31 | .2316 | 1.211 |
| 9 | .2016 | 1.054 | 32 | .2324 | 1.215 |
| 10 | .2034 | 1.063 | 33 | .2330 | 1.219 |
| 11 | .2052 | 1.073 | 34 | .2337 | 1.222 |
| 12 | .2069 | 1.082 | 35 | .2343 | 1.223 |
| 13 | .2087 | 1.092 | 36 | .2348 | 1.228 |
| 14 | .2104 | 1.100 | 37 | .2353 | 1.231 |
| 15 | .2120 | 1.109 | 38 | .2358 | 1.233 |
| 16 | .2136 | 1.117 | 39 | .2361 | 1.234 |
| 17 | .2152 | 1.126 | 40 | .2366 | 1.237 |
| 18 | .2167 | 1.133 | 41 | .2370 | 1.240 |
| 19 | .2182 | 1.141 | 42 | .2373 | 1.241 |
| 20 | .2196 | 1.149 | 43 | .2377 | 1.243 |
| 21 | .2210 | 1.156 | 44 | .2380 | 1.245 |
| 22 | .2223 | 1.162 | | | |
| *Operational Error (Incomplete oxygen charge) | | | | | |
| Specimen Temperature | | | 780°C | | |
| Point of Saturation (Rs) | | | Rs = .2310, $R_s/R_o = 1.205$ | | |
| Charge Size | | | 300 cc at 1000 μ pressure | | |
| Specimen Mass | | | 3.689 grams | | |
| Engassing Schedule | | | 3 3/4 min. engassing time followed by 3 3/4 min. homogenize time | | |
| Sample Preparation | | | Std procedure except for omission of 1450°C bake out | | |

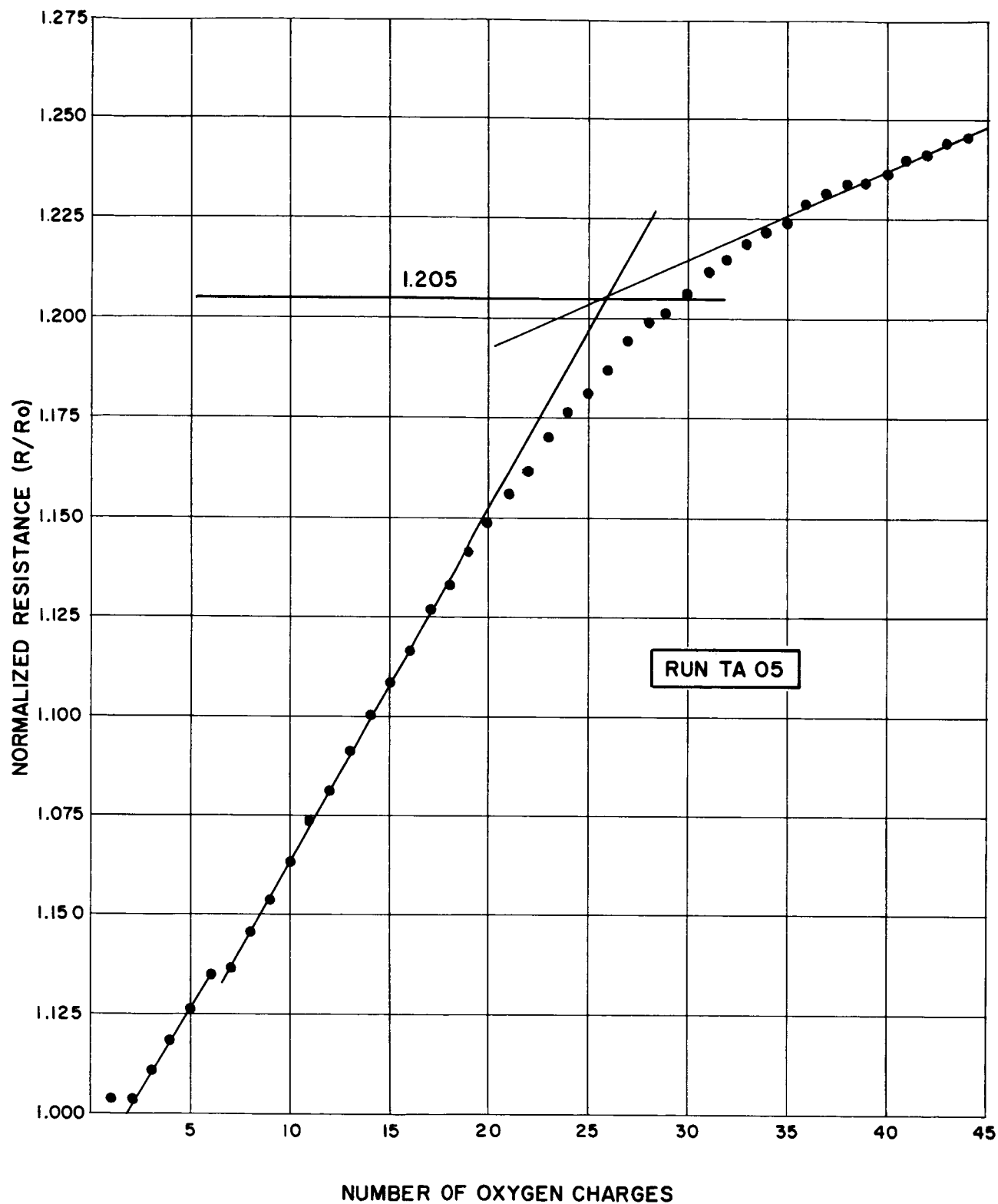


FIGURE 3. Plot of Normalized Resistance (R/R_o) versus number of oxygen charges for Run TA 05. The Run was at 780°C . See Table II and Text for additional details.

TABLE NO. III

| Resistance Data From Run TA 06 | | | | | |
|--------------------------------|----------|--------------------|---|----------|--------------------|
| Oxygen Charge No. | R (Ohms) | Normal-ized R R/Ro | Oxygen Charge No. | R (Ohms) | Normal-ized R R/Ro |
| 0 (Ro) | .2468 | 1.00 | 17 | .3052 | 1.237 |
| 1 | .2503 | 1.015 | 18 | .3067 | 1.243 |
| 2 | .2544 | 1.031 | 19 | .3079 | 1.248 |
| 3 | .2587 | 1.048 | 20 | .3089 | 1.252 |
| 4 | .2631 | 1.066 | 21 | .3100 | 1.256 |
| 5 | .2676 | 1.084 | 22 | .3108 | 1.259 |
| 6 | .2719 | 1.102 | 23 | .3116 | 1.263 |
| 7 | .2758 | 1.118 | 24 | .3124 | 1.266 |
| 8 | .2798 | 1.134 | 25 | .3130 | 1.268 |
| 9 | .2836 | 1.149 | 26 | .3137 | 1.271 |
| 10 | .2871 | 1.163 | 27 | .3141 | 1.273 |
| 11 | .2906 | 1.177 | 28 | .3147 | 1.275 |
| 12 | .2940 | 1.191 | 29 | .3153 | 1.278 |
| 13 | .2969 | 1.203 | 30 | .3158 | 1.280 |
| 14 | .2995 | 1.214 | 31 | .3161 | 1.281 |
| 15 | .3017 | 1.222 | 32 | .3166 | 1.283 |
| 16 | .3036 | 1.230 | 33 | .3171 | 1.285 |
| Specimen Temperature | | | 881°C | | |
| Point of Saturation | | | $R_s = .3082 \quad R_s/R_o = 1.249$ | | |
| Charge Size | | | 300cc at 2000u pressure | | |
| Specimen Mass | | | 4.2314 grams | | |
| Engassing Schedule | | | 3 1/3 min. engassing time followed by 3 1/2 min homogenize time | | |
| Specimen Preparation | | | Std procedure | | |

the reaction tube. An intersection was observed in the resistance vs. oxygen charge plot at approximately $R/R_o = 1.049$. Though the size of the oxygen charge was reduced to $1/2$ the standard unit charge for this run, it was still too large in view of the low limit of solubility at this low temperature. See Table IV.

Experimental Run TA 08

TA 08 was conducted at the constant temperature of 918°C . The specimen was given an additional pre-treatment of 1 hour at 1450°C in vacuum. A total of 37 unit charges of oxygen were admitted to the reaction tube. An intersection was observed in the resistance vs. oxygen charge plot at approximately $R/R_o = 1.272$. See Table V.

Experimental Run TA 09

TA 09 was terminated before completion due to equipment failure.

C. Oxygen-Calibration Runs (TA 10 through TA 14)

In the iso-thermal solubility determination technique the point of saturation for a given temperature is determined by monitoring the change in the specimen's electrical resistance as successive oxygen charges are admitted to the furnace reaction tube. The oxygen concentration corresponding to the ratio of initial resistance, at temperature, to the resistance at the point of saturation (R_s/R_o) must then be determined to yield the saturation limit (in ppm

TABLE NO. IV

| Resistance Data From Run TA 07 | | | | | |
|--|----------|-------------------|-------------------|----------|-------------------|
| Oxygen Charge No. | R (Ohms) | Normalized R R/Ro | Oxygen Charge No. | R (Ohms) | Normalized R R/Ro |
| 0 (Ro) | .1838 | 1.000 | 13 | .1942 | 1.059 |
| 1 | .1847 | 1.005 | 14 | .1952 | 1.062 |
| 2 | .1859 | 1.011 | 15 | .1960 | 1.066 |
| 3 | .1872 | 1.018 | 16 | .1965 | 1.069 |
| 4 | .1885 | 1.026 | 17 | .1969 | 1.071 |
| 5 | .1895 | 1.031 | 18 | .1974 | 1.073 |
| 6 | .1906 | 1.037 | 19 | .1979 | 1.077 |
| 7 | .1912 | 1.040 | 20 | .1983 | 1.079 |
| 8 | .1920 | 1.045 | 21 | .1987 | 1.081 |
| 9 | .1924 | 1.047 | 22 | .1992 | 1.084 |
| 10 | .1931 | 1.051 | 23 | .1997 | 1.087 |
| 11 | .1937 | 1.054 | 24 | .2002 | 1.089 |
| 12 | .1942 | 1.057 | 25 | .2006 | 1.091 |
| <p>Specimen Temperature 598°C</p> <p>Point of Saturation $R_s = .1929, R_s/R_o = 1.049$</p> <p>Charge Size 300 cc at 1000u pressure</p> <p>Specimen Mass 4.0131 grams</p> <p>Engassing Schedule 3 3/4 min engassing time followed by 3 3/4 min. homogenize time</p> <p>Specimen Preparation Std procedure</p> | | | | | |

TABLE NO. V

| Resistance Data From Run TA 08 | | | | | |
|--|----------|---|-------------------|----------|--------------------|
| Oxygen Charge No. | R (Ohms) | Normal-ized R R/Ro | Oxygen Charge No. | R (Ohms) | Normal-ized R R/Ro |
| 0 Ro* | .1706 | 1.000 | 19 | .2186 | 1.281 |
| 1* | .1738 | 1.019 | 20 | .2192 | 1.285 |
| 2 | .1770 | 1.038 | 21 | .2197 | 1.288 |
| 3 | .1810 | 1.061 | 22 | .2203 | 1.291 |
| 4 | .1850 | 1.084 | 23 | .2207 | 1.294 |
| 5 | .1886 | 1.106 | 24 | .2211 | 1.296 |
| 6 | .1924 | 1.128 | 25 | .2215 | 1.298 |
| 7 | .1953 | 1.145 | 26 | .2219 | 1.301 |
| 8 | .1973 | 1.157 | 27 | .2222 | 1.302 |
| 9 | .2012 | 1.180 | 28 | .2225 | 1.304 |
| 10** | .2039 | 1.195 | 29 | .2229 | 1.307 |
| 11 | .2067 | 1.212 | 30 | .2233 | 1.309 |
| 12 | .2089 | 1.225 | 31 | .2237 | 1.311 |
| 13 | .2110 | 1.237 | 32 | .2240 | 1.313 |
| 14 | .2129 | 1.248 | 33 | .2244 | 1.315 |
| 15 | .2145 | 1.257 | 34 | .2247 | 1.317 |
| 16 | .2158 | 1.265 | 35 | .2250 | 1.389 |
| 17 | .2169 | 1.271 | 36 | .2254 | 1.321 |
| 18 | .2178 | 1.278 | | | |
| * Seven min. delay due to T.C. meter sticking **Closed high vacuum valve with one min. early. | | | | | |
| Specimen Temperature | | 918°C | | | |
| Point of Saturation | | $R_s = .2171$ $R_s/R_o = 1.272$ | | | |
| Charge Size | | 300 cc at 1000 μ pressure | | | |
| Specimen Mass | | 3.4180 grams | | | |
| Engassing Schedule | | 3 3/4 min. engassing followed by 3 3/4 min. | | | |
| Specimen Preparation | | Std procedure except for 1450°C bake out | | | |

of oxygen) for the particular temperature. Therefore a series of experimental runs was conducted to determine the relation between R/R_o of a sample material and its oxygen content (in ppm) in the range below saturation.

Five oxygen calibration runs were conducted (TA 10 to TA 14) and the engassing data are reported in Tables VI through X. In each case the specimen was cleaned per standard procedure and vacuum baked overnight at 900°C. Four of the specimens were engassed (300 cc at 2000 μ of oxygen per charge, 7 - 1/2 minute cycle) to various values of R/R_o in the range of interest; the fifth specimen (TA 13) was not engassed. These five specimens together with an "as received" sample of the Ta material and two specimens from previous runs were submitted for neutron activation analysis for oxygen content.

The report of the activation analysis service is tabulated in Table XI and is plotted against R/R_o in Figure 4.

These results, although good, are not up to the expected accuracy; it had been hoped that 10 ppm accuracy would be obtained. The standard deviation is 50 ppm as determined from counting statistics. This discrepancy is perhaps due to the form of specimen, in that the wire did not fill the neutron activation analysis capsule volume. The inertia of the material kept it at the trailing end

TABLE NO. VI

| Resistance Data From Run TA 10 | | | | | |
|--|----------|-------------------------------|-------------------|----------|-------------------------------|
| Oxygen Charge No. | R (Ohms) | Normalized R R/R ₀ | Oxygen Charge No. | R (Ohms) | Normalized R R/R ₀ |
| 0 (R ₀) | .2081 | 1.000 | 4 | .2236 | 1.075 |
| 1 | .2113 | 1.016 | 5 | .2277 | 1.095 |
| 2 | .2154 | 1.036 | 6 | .2321 | 1.116 |
| 3 | .2195 | 1.055 | | | |
| <p>Specimen Temperature 899°C</p> <p>Point of Saturation NONE (O₂ Calibration Run)</p> <p>Charge Size 300 cc at 2000μ pressure</p> <p>Specimen Mass 3.6060 grams</p> <p>Engassing Schedule 3 3/4 min. engassing followed by 3 3/4 min. homogenize time</p> <p>Specimen Preparation Std procedure</p> | | | | | |

TABLE NO. VII

| Resistance Data From Run TA 11 | | | | | |
|--------------------------------|----------|--------------------|-------------------|----------|--------------------|
| Oxygen Charge No. | R (Ohms) | Normal-ized R R/Ro | Oxygen Charge No. | R (Ohms) | Normal-ized R R/Ro |
| 0 (Ro) | .2207 | 1.000 | 3 | .2318 | 1.050 |
| 1 | .2240 | 1.015 | | | |
| 2 | .2279 | 1.003 | | | |

| | |
|----------------------|---|
| Specimen Temperature | 901°C |
| Point of Saturation | NONE (O ₂ Calibration Run) |
| Charge Size | 300 cc at 2000μ pressure |
| Specimen Mass | 3.9193 grams |
| Engassing Schedule | 3 3/4 min. engassing followed by 3 3/4 min. homogenize time |
| Specimen Preparation | Std procedure |

TABLE NO. VIII

| Resistance Data From Run TA 12. | | | | | |
|---|----------|-------------------|-------------------|----------|-------------------|
| Oxygen Charge No. | R (Ohms) | Normalized R R/Ro | Oxygen Charge No. | R (Ohms) | Normalized R R/Ro |
| 0 (Ro) | .2271 | 1.000 | 6 | .2517 | 1.108 |
| 1 | .2305 | 1.015 | 7 | .2558 | 1.126 |
| 2 | .2344 | 1.032 | 8 | .2598 | 1.144 |
| 3 | .2386 | 1.051 | 9 | .2637 | 1.161 |
| 4 | .2429 | 1.070 | 10 | .2678 | 1.179 |
| 5 | .2473 | 1.089 | 11 | .2680 | 1.180 |
| <p>Specimen Temperature 898°C</p> <p>Point of Saturation NONE (O₂ Calibration Run)</p> <p>Charge Size 300cc at 2000u pressure</p> <p>Specimen Mass 4.0417 grams</p> <p>Engassing Schedule 3 3/4 min. engassing followed by 7 1/2 min homogenize time</p> <p>Specimen Preparation Std procedure</p> | | | | | |

TABLE NO. IX

| Resistance Data From Run TA 13 | | | | | |
|---|----------|-------------------------------|-------------------|----------|-------------------------------|
| Oxygen Charge No. | R (Ohms) | Normalized R R/R ₀ | Oxygen Charge No. | R (Ohms) | Normalized R R/R ₀ |
| (NONE) R ₀ | .2238 | 1.000 | | | |
| <p>Specimen Temperature 901°C</p> <p>Point of Saturation NONE (No Engassing)</p> <p>Charge Size NONE</p> <p>Specimen Size 4.0262 grams</p> <p>Engassing Schedule NONE</p> <p>Specimen Preparation Std procedure</p> | | | | | |

TABLE NO. X

| Resistance Data From Run TA 014 | | | | | |
|---------------------------------|----------|--------------------------------|-------------------|----------|--------------------------------|
| Oxygen Charge No. | R (Ohms) | Normal-ized R R/R ₀ | Oxygen Charge No. | R (Ohms) | Normal-ized R R/R ₀ |
| 0 (R ₀) | .2483 | 1.000 | 8 | .2892 | 1.165 |
| 1 | .2542 | 1.024 | 9 | .2912 | 1.176 |
| 2 | .2602 | 1.048 | 10 | .2950 | 1.188 |
| 3 | .2661 | 1.072 | 11 | .2977 | 1.199 |
| 4 | .2717 | 1.094 | 12 | .2997 | 1.207 |
| 5 | .2769 | 1.115 | 13 | .3019 | 1.216 |
| 6 | .2814 | 1.133 | 14 | .3032 | 1.221 |
| 7 | .2854 | 1.149 | 15 | .3045 | 1.226 |

| | |
|----------------------|--|
| Specimen Temperature | 900°C |
| Point of Saturation | NONE (O ₂ Calibration Run) |
| Charge Size | 300cc at 2000u pressure |
| Specimen Mass | 4.0368 grams |
| Engassing Schedule | 3 3/4 min. Engassing followed by 3 3/4 min. homogenize |
| Specimen Preparation | Std procedure |

TABLE XI

| Neutron Activation Analysis For Oxygen (ppm) | | | | | |
|--|--------|------------------|--|------|-----------|
| SPECIMEN | WT (g) | R/R _O | Oxygen ppm 1st & 2nd Determination | | Std. Dev. |
| As Received | 3.1523 | ---- | 159 | 133 | 20 |
| TA-13 | 2.6639 | 1.0000 | 206 | 225 | 20 |
| TA-11 | 2.6425 | 1.0507 | 817 | 764 | 50 |
| TA-10 | 2.4341 | 1.1163 | 1350 | 1300 | 50 |
| TA-12 | 2.7401 | 1.1792 | 1640 | 1710 | 60 |
| TA-14 | 2.6231 | 1.3035 | 2440 | 2490 | 50 |
| TA-05** | 2.5182 | 1.2447 | 4370 | 4370 | 40 |
| TA-07** | 2.8456 | 1.1147 | 2450 | 2430 | 10 |
| **Included here for comparison | | | | | |

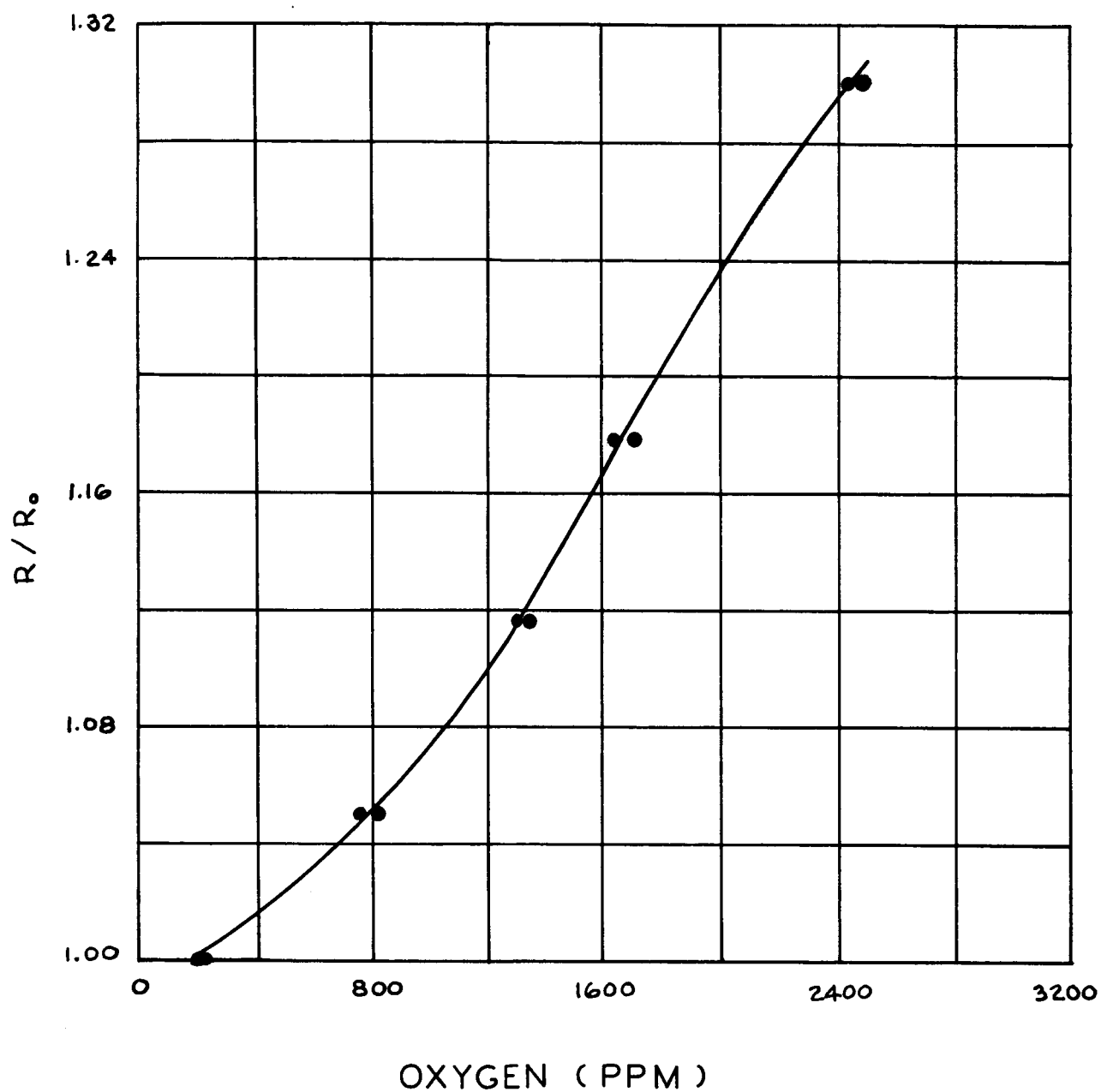


FIGURE 4. Calibration Curve for Oxygen in Tantalum in terms of normalized electrical resistance (R/R_0) of the tantalum. Samples were engassed at $900^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

of the capsule as it was shot toward the neutron counters thereby passing the counters later than the leading end of the capsule. Further, specimens were deformed or fragmented by the 1st pass so that the geometry is different for the 2nd pass.

D. Extended Time Solubility Experiments

Three runs were completed whose main objective was to determine the effect of extending the length of the cycle in iso-thermal experiments (TA15, TA16) or employing a lower cooling rate in an iso-concentration experiment (TA17). All three specimens were heated in vacuum at 1450°C for one hour in addition to the standard pre-treatment of 900°C in vacuum overnight. This alteration in pre-treatment did not affect the final result significantly, (see later).

Iso-Thermal Runs TA 15 and TA 16

The iso-thermal experiments TA 05 to TA 09 employed either a 7 - 1/2 minute engassing cycle with a full "unit" (300 cc at 2000 μ) or a "half-unit" charge. Runs TA 15 and TA 16 employed a 30 minute cycle (3-3/4 minutes engassing time with 26-1/4 minutes for homogenization in vacuo at 780°C.) The specimens used in these runs were annealed at 1450°C for one hour, by self heating, before engassing.

Run TA 15 was terminated after 18 engassing cycles due to equipment failure.

Run TA 16 was carried to completion and a "curve

break" inflection occurred at $R/R_o = 1.198$, Figure 5.

Data are reported in Table XII.

Iso-Concentration Run TA 17

Previous iso-concentration runs reported in the 2nd Quarterly Report at average cooling rates of approximately $2^{\circ}\text{C}/\text{minute}$ had failed to produce a discernable inflection. Run TA 17 was engassed using the standard 7-1/2 minute cycle and unit charges. This iso-concentration experimental run was then programmed to determine whether an inflection in the resistance vs temperature curve would occur if the average cooling rate were reduced to $0.83^{\circ}\text{C}/\text{min}$. This was accomplished by manually lowering the specimen temperature in 25°C steps every 30 minutes.

The resistance values obtained from this run were plotted. There was little or no change in resistance noted after reaching temperature for any given step. There was no discernable inflection in the resistance vs temperature curve. Data on the engassing schedule and the temperature cycle are repeated in Tables XIII and XIV.

Note on Equilibrium of Oxygen with Tantalum

Three resistance measurements were made during each engassing cycle during runs TA 15 and TA 16; one at approximately 4 minutes, after the pressure in the reaction tube had fallen back to the "base-pressure" level, another within a minute of the end of the 30 minute cycle; and one

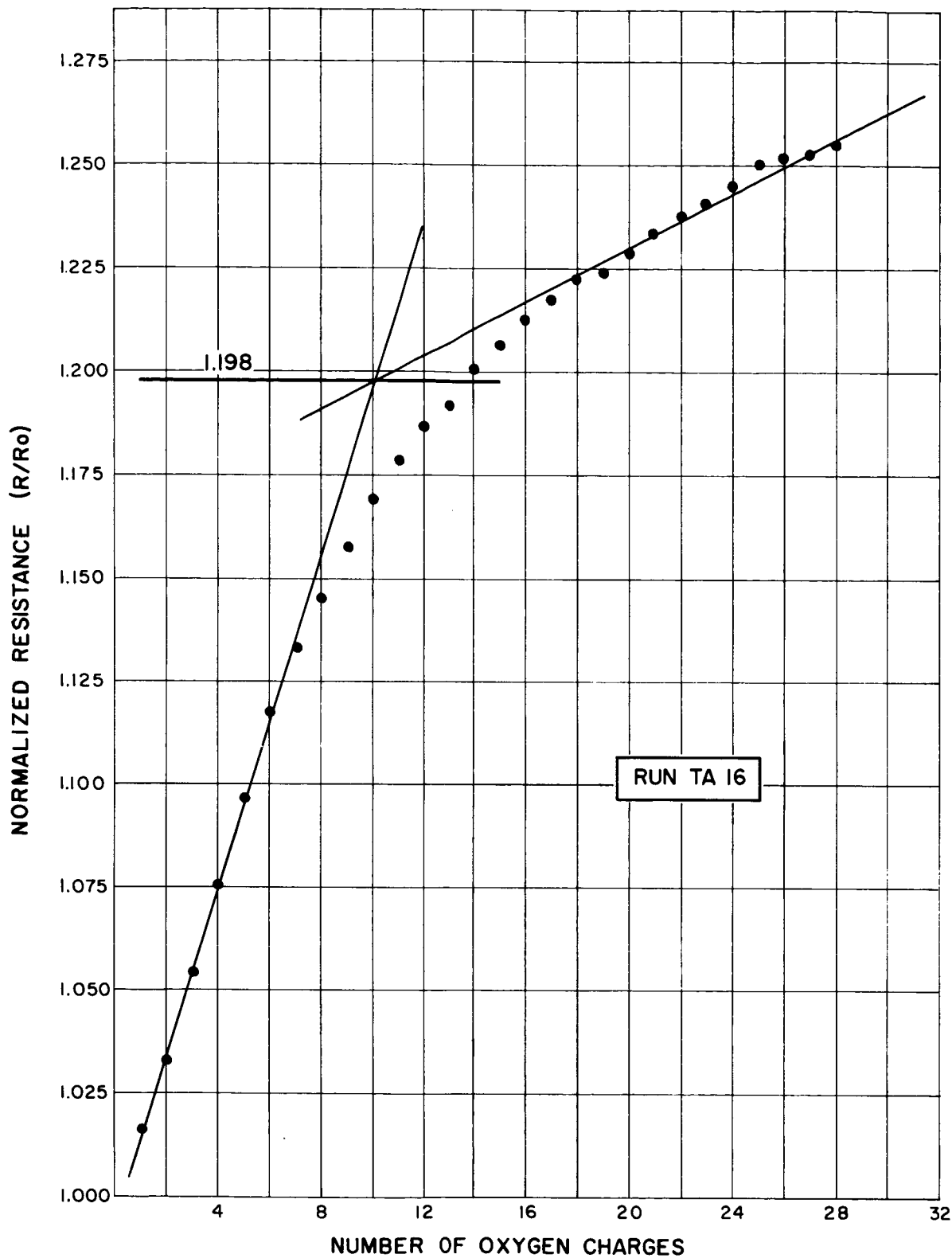


FIGURE 5. Plot of Normalized Resistance (R/R_o) versus Number of Oxygen Charges for Run TA 16. The Run was at 780°C with extended hold times between oxygen charges. See Table XII and Text for additional details.

TABLE NO. XII

| Resistance Data From TA 16 | | | | | |
|---|----------|-------------------------------|-------------------|----------|-------------------------------|
| Oxygen Charge No. | R (Ohms) | Normalized R R/R ₀ | Oxygen Charge No. | R (Ohms) | Normalized R R/R ₀ |
| 0 | .1578 | 1.000 | 15 | .1904 | 1.207 |
| 1 | .1598 | 1.017 | 16 | .1914 | 1.213 |
| 2 | .1630 | 1.033 | 17 | .1922 | 1.218 |
| 3 | .1665 | 1.055 | 18 | .1930 | 1.223 |
| 4 | .1698 | 1.076 | 19 | .1932 | 1.224 |
| 5 | .1731 | 1.097 | 20 | .1940 | 1.229 |
| 6 | .1764 | 1.118 | 21 | .1947 | 1.234 |
| 7 | .1790 | 1.134 | 22 | .1954 | 1.238 |
| 8 | .1807 | 1.145 | 23 | .1959 | 1.241 |
| 9 | .1828 | 1.158 | 24 | .1964 | 1.245 |
| 10 | .1844 | 1.169 | 25 | .1971 | 1.250 |
| 11 | .1860 | 1.179 | 26 | .1975 | 1.252 |
| 12 | .1873 | 1.187 | 27 | .1978 | 1.253 |
| 13 | .1883 | 1.193 | 28 | .1982 | 1.256 |
| 14 | .1895 | 1.201 | | | |
| <div> <div>Specimen Temperature</div> <div>780°C</div> </div> <div> <div>Point of Saturation</div> <div>$R_s = 1.890$ $R_s/R_0 = 1.198$</div> </div> <div> <div>Charge Size</div> <div>300 cc at 2000μ pressure</div> </div> <div> <div>Specimen Mass</div> <div>3.665 grams</div> </div> <div> <div>Engassing Schedule</div> <div>3 3/4 min. engassing time followed by 25 min. homogenizing time.</div> </div> <div> <div>Specimen Preparation</div> <div>Std procedure except for 1450°C bake out.</div> </div> | | | | | |

TABLE NO. XIII

| Resistance Data From Run TA 17 | | | | | |
|---|----------|-------------------|-------------------|----------|-------------------|
| Oxygen Charge No. | R (Ohms) | Normalized R R/Ro | Oxygen Charge No. | R (Ohms) | Normalized R R/Ro |
| Ro (Ro) | .1995 | 1.000 | 7 | .2314 | 1.160 |
| 1 | .2077 | 1.041 | 8 | .2352 | 1.179 |
| 2 | .2093 | 1.049 | 9 | .2394 | 1.198 |
| 3 | .2151 | 1.078 | 10 | .2429 | 1.218 |
| 4 | .2213 | 1.109 | 11 | .2455 | 1.231 |
| 5 | .2246 | 1.126 | 12 | .2487 | 1.247 |
| 6 | .2283 | 1.144 | | | |
| <p>Specimen Temperature 901°C</p> <p>Point of Saturation NONE (Sample used for iso-concentration Run) See Table XIV</p> <p>Charge Size: 300cc at 2000μ pressure</p> <p>Specimen Mass: 3.655 grams</p> <p>Engassing Schedule 3 3/4 min. engassing time followed by 3 3/4 min homogenize time</p> <p>Specimen Preparation Std procedure except for 1450°C bake out</p> | | | | | |

TABLE NO. XIV

| Iso-Concentration Data From Run TA 17 | | |
|--|-------------------------|---------------------------------|
| Event No. | Specimen Temperature °C | Resistance After 30 Minute Hold |
| 1 | 950 | .2250 |
| 2 | 924.9 | .2510 |
| 3 | 900.6 | .2480 |
| 4 | 874.8 | .2442 |
| 5 | 850.7 | .2406 |
| 6 | 825.4 | .2366 |
| 7 | 801.5 | .2329 |
| 8 | 744.1 | .2287 |
| 9 | 752.4 | .2255 |
| 10 | 724.1 | .2210 |
| 11 | 702.9 | .2174 |
| Cooling Rate: 250°C/300 min. Charge Size: NONE Specimen Mass: 3.6551 grams Specimen Preparation: Std procedure except for 1450°C bake out | | |

measurement between these two. There was a small difference between the three readings due to experimental procedure. There was a slight increase in resistance; at many engassing levels above saturation, the three readings are in agreement. Table XV shows typical values of the resistance fluctuation at various engassing levels (for TA 16).

E. Tentative Solubility Limits for Oxygen in Ta.

Figure 6 is a tentative plot of solubility limit vs temperature as determined from iso-thermal experimental runs TA 05, TA 06, TA 07, and TA 08 as well as from TA 16 (extended time iso-thermal run). No TA 17 data representing an iso-concentration run is presented since no readily discernable indication of solubility limit was obtained from TA 17 or from runs TA 01*, TA 03*, and TA 04*.

The values for oxygen in ppm were obtained by referencing the value of R/R_0 for an individual run against the oxygen calibration curve (Figure 4). The error limits shown in Figure 4 are those associated with the neutron activation analysis alone. The error in temperature is estimated at less than $\pm 2^\circ\text{C}$ and so is the lesser of the two**. After oxygen analysis the second greatest source of error is that associated with the determination of the R/R_0 value at saturation for each individual iso-thermal run; this is a graphical solution for the intersection of two straight line segments which themselves are a graphical approximation.

*Reported in Second Quarterly Report.

** $\Delta T = 1^\circ\text{C}$ is equivalent to $\Delta O_2 = 8 \text{ ppm Max.}$ from the graphical plot of the data.

TABLE XV

| Resistance Variation As A Function Of Time | | | | |
|--|-------------------|----------------|----------------|--------|
| At Constant Oxygen Levels* | | | | |
| Oxygen Charge No. | Resistance (Ohms) | | | |
| | R ₁ | R ₂ | R ₃ | ΔR |
| 1 | .1598 | .1599 | .1600 | +.0002 |
| 2 | .1630 | .1631 | .1632 | +.0002 |
| 3 | .1665 | .1667 | .1667 | +.0002 |
| 4 | .1698 | .1699 | .1702 | +.0004 |
| 5 | .1731 | .1732 | .1732 | +.0001 |
| 6 | .1764 | .1764 | .1765 | +.0001 |
| 7 | .1790 | .1790 | .1790 | .0000 |
| 8 | .1807 | .1809 | .1810 | +.0003 |
| 9 | .1828 | .1828 | .1828 | .0000 |
| 10 | .1844 | .1945 | .1845 | +.0001 |
| 11 | .1860 | .1860 | .1860 | .0000 |
| 12 | .1873 | .1873 | .1873 | .0000 |
| 13 | .1881 | .1883 | .1883 | +.0002 |
| 14 | .1895 | .1895 | .1895 | .0000 |
| 15 | .1904 | .1904 | .1905 | +.0001 |
| 16 | .1914 | .1914 | .1914 | .0000 |
| 17 | .1921 | .1922 | .1922 | +.0001 |
| 18 | .1929 | ----- | .1930 | +.0001 |
| 19 | .1932 | ----- | .1932 | .0000 |
| 20 | ----- | .1939 | .1940 | +.0001 |
| 21 | ----- | .1946 | .1947 | +.0001 |
| 22 | ----- | .1954 | .1954 | .0000 |
| 23 | ----- | ----- | .1959 | ----- |
| 24 | .1964 | .1964 | .1964 | .0000 |
| 25 | .1970 | .1971 | .1971 | +.0001 |
| 26 | ----- | ----- | .1975 | ----- |
| 27 | ----- | ----- | .1977 | ----- |
| 28 | ----- | .1981 | .1982 | +.0001 |
| R ₁ Initial Resistance after Engassing | | | | |
| R ₂ Resistance at Intermediate Point in Time | | | | |
| R ₃ Resistance After 26 1/4 min. Homogenization | | | | |
| *DATA FROM EXTENDED TIME SOLUBILITY RUN TA 16 | | | | |

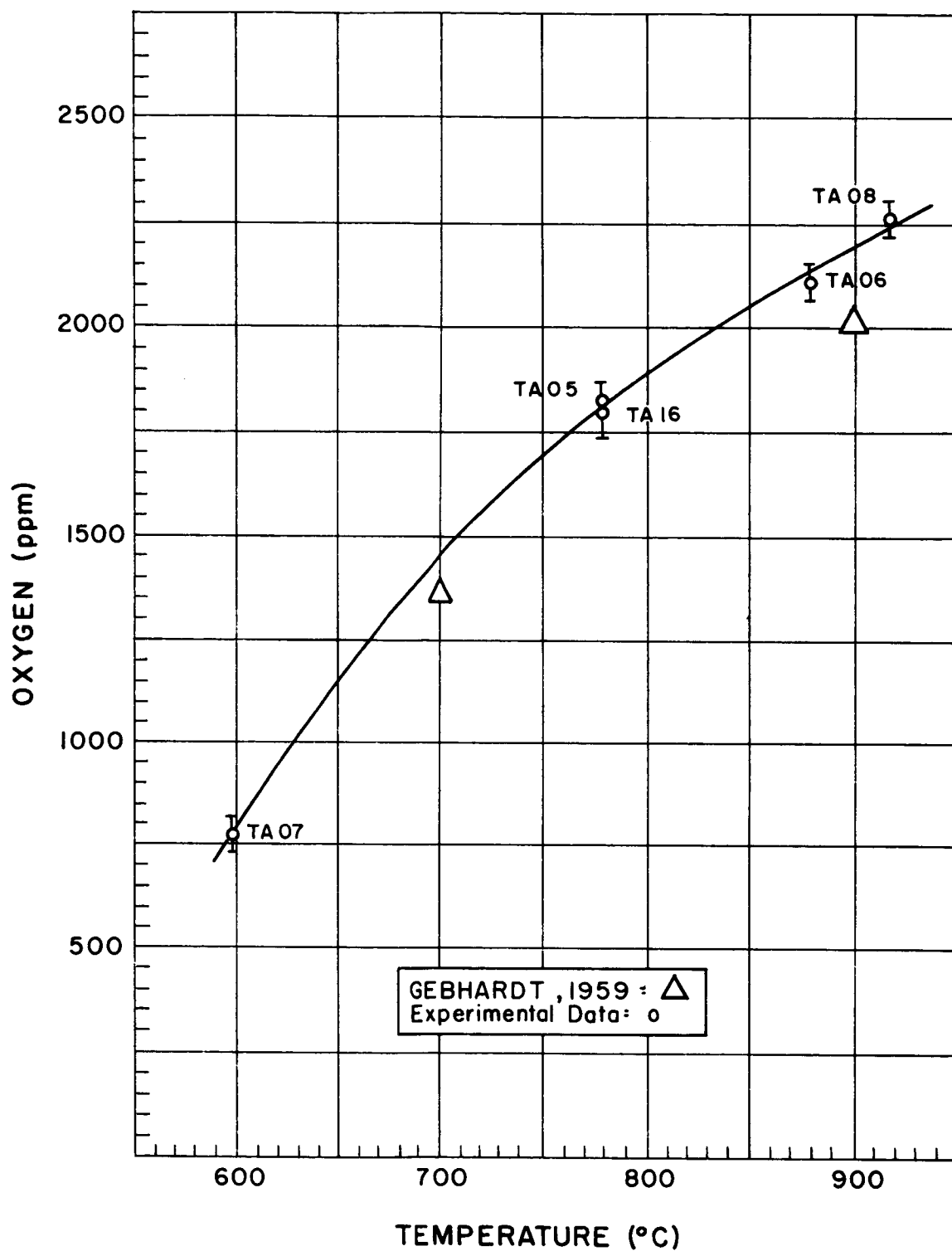


FIGURE 6. Plot of Oxygen Solubility versus Temperature for Tantalum (tentative).

Because neutron activation analysis is capable of a higher degree of accuracy than that realized herein and since the graphical error has not yet been evaluated, the solubility limits reported here will be considered tentative.

VI. DISCUSSIONS AND CONCLUSIONS

A. Extended time Solubility Runs

Iso-thermal run TA 05 indicated a saturation limit of 1835 ppm of oxygen at 780°C ($R/R_o = 1.204$) while iso-thermal run TA 16 (extended time cycle) indicated a saturation limit of 1795 ppm of oxygen at 781° ($R/R_o = 1.198$). Discounting the difference in (constant) temperature the values are within 40 ppm as compared to the neutron activation analysis standard deviation of ± 50 ppm at that range.

The longer engassing time should allow the Ta-O₂ system to more closely approach an equilibrium resistance value. It was therefore anticipated that Run TA 16 would indicate the same or a greater O₂ solubility, as compared to TA 05. The decrease in solubility with increased homogenizing time indicates that one of at least three things are happening.

1. Since the homogenization is taking place in high vacuum with a very low oxygen partial pressure, there is a net loss in oxygen during the hold time due to outgassing which increases with longer hold times.

2. A compositional or metallurgical change is taking place which affects the overall electrical resistivity of the specimen such as grain boundary oxide spheroidization.

3. The temperature error is of an order of $\pm 2^{\circ}\text{C}$ which would be about ± 16 ppm. In addition, the higher temperature anneal at 1450°C for TA 16 may have contributed to the difference.

Three resistance measurements were made during the homogenization portion (26-1/4 minutes) of each engassing cycle (See Table XV). Were the resistance values obtained from an iso-thermal run time dependent, the three values for each cycle would show a consistent trend; they do not.

The resistance fluctuation is attributed mainly to small ($\pm 2^{\circ}\text{C}$) temperature variations and possibly resistance measurement errors, the latter is extremely small. The effect of possible time dependence on the final value of R/R_0 for the saturation point can best be determined when a computer program is available for evaluating iso-thermal data. (The data from TA -16 used in determining the tentative solubility limits reported above was obtained by using the third (final) resistance measurement from each engassing cycle. The failure of the iso-concentration method (run TA 17) to produce a graphically discernable inflection at the temperature corresponding to the saturation limit for the

dissolved oxygen level present, indicates that this technique is not feasible, at least for Ta, within the objectives and scope of this program. An additional continuous temperature rate programmer is needed in order to pursue this technique further.

B. Computer Programs

Both the iso-thermal and the iso-concentration methods employed rely on graphical solutions to determine points of saturation; this dependence introduces a small systematic error. To obviate graphical solutions, it is desirable to develop computer programs to process the raw data and locate the saturation point.

Results to date with the iso-concentration technique yield no apparent indication of a saturation point in the plotted data. If, indeed, the dissolved oxygen is not totally "frozen-in" but does precipitate in some finite amount, then the saturation point can only be determined (for Ta, at least) by a statistical analysis. A simple single regression program was written and applied to the data from iso-concentration runs with unsatisfactory results to date. A multiple regression analysis would be more in order (e.g., an adaptation of the NASA SNAP 7094 Regression Analysis Program) and will be considered for future use.

In the case of the iso-thermal technique the indications of the point of saturation are real and easily discernable

from the plotted data. The tentative solubility limits reported above are derived from a graphical solution and are subject to an uncertain error. A computer program could be used to calculate the error in the extrapolation process and define the saturation point with less uncertainty. Preliminary work has begun in this area; a simple program has been written and applied to test cases.

VII. WORK PLANNED FOR NEXT QUARTER

1. Further analysis of the data from all trial runs, solubility determination runs and oxygen calibration runs.
2. Determination of solubility limits of oxygen in columbium in the range 580°C to 950°C.
3. Process additional alumina reaction tubes and place high temperature oxygen solubility furnace in operation. If the present tubes cannot be successfully metallized, order tubes from a second source known to have the capacity of being metallized. (AD-99 or AD995, Coors).
4. Continue design and construction of diffusion apparatus.
5. Develop computer program to determine saturation points from iso-thermal experimental data.